

7806

(12) **UK Patent Application** (19) **GB** (11) **2 311 296** (13) **A**

(43) Date of A Publication 24.09.1997

(21) Application No 9705617.0

(22) Date of Filing 18.03.1997

(30) Priority Data

(31) 08590551  
08770194

(32) 19.03.1996  
20.12.1996

(33) US

(71) Applicant(s)

**The Procter & Gamble Company**

**(Incorporated in USA - Ohio)**

**One Procter & Gamble Plaza, Cincinnati, Ohio 45202,  
United States of America**

(72) Inventor(s)

**Toan Trinh**

**Dennis R Bacon**

**Patricia A Blondin-Cook**

**Alex H Chung**

(51) INT CL<sup>6</sup>

**C11D 3/50 // (C11D 3/50 1:02 1:12 3:02 3:06 3:065 3:08  
3:10)**

(52) UK CL (Edition O)

**CSD DHD D107 D108 D110 D111 D120 D123 D129 D142  
D149 D153 D180**

(56) Documents Cited

**GB 2303789 A EP 0430315 A2 EP 0392608 A2  
EP 0299561 A2 WO 95/13345 A1 WO 93/05136 A1**

(58) Field of Search

**UK CL (Edition O) CSD DHD DHZ DJX  
INT CL<sup>6</sup> C11D  
Online: WPI**

(74) Agent and/or Address for Service

**Elkington and Fife**

**Prospect House, 8 Pembroke Road, SEVENOAKS,  
Kent, TN13 1XR, United Kingdom**

**(54) Perfumed particulate detergent compositions for hand dishwashing**

**(57) Disclosed are perfumed, dry particulate detergent and detergent/bleach compositions comprising anionic surfactant; solid builder and/or filler materials; and a blooming perfume composition. The components of the blooming perfume composition are defined by their boiling point and their octanol/water partition coefficient. Such compositions, which optionally contain a chlorine bleach, are useful for the hand washing of cooking and/or eating utensils. The perfume component utilized therein is readily noticeable to the user of the composition but does not spot or film surfaces washed using such compositions.**

**GB 2 311 296 A**

**Title: PERFUMED, PARTICULATE DETERGENT COMPOSITIONS**  
**FOR HAND DISHWASHING**

The present invention relates to particulate dry detergent compositions and detergent with bleach compositions which are useful for the hand washing of eating and cooking utensils and which have an especially desirable perfume composition incorporated thereinto.

In many parts of the world, granular detergent products, which contain relatively high levels of surfactants, builders and preferably bleaching agents, are used for the hand washing of eating and cooking utensils. Since dishwashing operations using such products involve the close proximity of the dishwasher to the dishwashing operation and to the detergent products used therein, it is desirable and commercially beneficial to add perfume materials to such products. Perfumes provide an olfactory aesthetic benefit that can serve as a signal of cleanliness. Such perfumes should therefore be readily noticeable to the user of the particulate dishwashing products. Any perfumes that are used, however, should not leave residue or residual odor on surfaces that the washing solution formed from any such product has contacted. Residual perfumes on such surfaces, for example, on pots, pans, dishes and countertops, can cause undesirable spotting and filming.

Given the foregoing considerations, it is an object of the present invention to provide perfumed, dry particulate detergent compositions suitable for use in hand dishwashing operations for the cleaning of eating and cooking utensils.

It is a further object of this invention to provide in such perfumed hand dishwashing products selected types of "blooming" perfume ingredients which impart a readily noticeable and desirable odor to the dishwashing products during use.

It is a further object of the present invention to provide such blooming perfumed detergent products that do not leave undesirable residual spotting or

filming perfume materials on surfaces contacted with washing solutions formed from such products.

The present invention provides perfumed, dry particulate detergent compositions which are useful for the hand washing of eating and cooking utensils and which have an especially desirable and noticeable blooming perfume component. Such compositions comprise a) at least about 1% of an anionic surfactant; b) sufficient builder and filler to ensure a dry particulate composition; and c) from about 0.05% to 3% of a blooming perfume composition. The blooming perfume composition is one which contains at least five different blooming perfume ingredients. A blooming perfume ingredient is one which has a boiling point of 260°C or lower and which has a calculated  $\log_{10}$  of its octanol/water partition coefficient,  $P$ , of about 3 or higher. Such compositions preferably also contain a chlorine bleach and have their blooming perfume compositions protected by combining the perfume composition with other materials to form moisture-activated, encapsulated perfume particles. When the blooming perfume composition is present in the form of cyclodextrin/perfume complexes, particles of such complexes should be no more than about 12 microns in size.

Materials essentially and optionally incorporated in the detergent and bleach compositions of the present invention are described hereinafter. Unless otherwise specified, all concentrations and ratios are on a weight basis.

The compositions described herein are "dry particulate" products. For purposes of this invention, "dry particulate" compositions are not necessarily moisture-free, but are flowable powder or granular products which are essentially dry to the touch.

As used herein, "alkyl" means hydrocarbyl moieties which are straight or branched, saturated or unsaturated with one or more double bonds. Alkyl may be of single or mixed lengths, and are often mixed lengths and saturation derived from natural sources such as tallow, coconut oil, palm oil, etc.

#### **Anionic Surfactants**

The compositions herein comprise at least about 1%, preferably at least about 8%, also preferably at least about 18% anionic surfactant, more preferably from about 20% to about 40%, more preferably still from about 22% to about 36%, more preferably still from about 24% to about 32%, still more preferably from about 26% to about 30%.

Preferred anionic surfactant materials useful in the subject compositions include the water-soluble salts, preferably the alkali metal, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to about 24 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of such anionic surfactants are the salts of compatible cations, e.g., sodium, potassium, ammonium, monoethanolammonium, diethanolammonium, and triethanolammonium, with alkyl sulfates, alkylbenzene or alkyltoluene sulfonates, ethoxylated alkyl sulfates, and other surfactant anions disclosed hereinbelow.

Preferred alkylbenzene and alkyltoluene sulfonates include those with an alkyl portion which is straight chain or branched chain, preferably having from about 8 to 18 carbon atoms, more preferably from about 10 to about 16 carbon atoms. The alkyl chains of the alkylbenzene and alkyltoluene sulfonates preferably have an average chain length of from about 11 to about 14 carbon atoms. Alkylbenzene sulfonates are preferred. Alkylbenzene sulfonate which includes branched chain alkyl is termed ABS. Alkylbenzene sulfonate which is all straight chain is preferred because it is more biodegradable; it is termed LAS and is the preferred anionic surfactant. Alkylbenzene sulfonic acids useful as precursors for these surfactants include decylbenzene sulfonic acid, undecylbenzene sulfonic acid, dodecylbenzene sulfonic acid, tridecylbenzene sulfonic acid, tetrapropylenebenzene sulfonic acid, and mixtures thereof. Preferred sulfonic acids as precursors of the alkylbenzene sulfonates useful for compositions herein are those in which the alkyl chain is linear and averages from about 11 to about 13 carbon atoms in length. Suitable cations for such alkylbenzene sulfonates include the alkali metals (lithium, sodium, and potassium), ammonium and/or alkanolammonium; preferred are potassium, and especially sodium.

Preferred alkyl sulfates include those with an alkyl portion which is straight chain or branched chain, preferably having from about 8 to about 24 carbon atoms, more preferably from about 10 to about 20 carbon atoms, more preferably still from about 12 to about 18 carbon atoms. The alkyl chains of the alkyl sulfates preferably have an average chain length of from about 14 to about 16 carbon atoms. The alkyl chains are preferably linear. Alkyl sulfates are typically obtained by sulfating fatty alcohols produced by reducing the glycerides of fats and/or oils from natural sources, especially from tallow or coconut oil. Preferred alkyl sulfates include lauryl sulfates, stearyl sulfates, palmityl sulfates, decyl sulfates, myristyl sulfates, tallow alkyl sulfates, coconut alkyl sulfates, C<sub>12-15</sub> alkyl sulfates, and mixtures of these surfactants. Preferred cations for the alkyl sulfates include sodium, potassium,

ammonium, monoethanolammonium, diethanolammonium, and triethanolammonium; most preferred is sodium.

Other preferred anionic surfactants include alkylpolyethoxylate sulfates having the formula  $\text{RO}(\text{C}_2\text{H}_4\text{O})_X\text{SO}_3\text{M}$  wherein R is alkanyl or alkenyl having from about 10 to about 20 carbon atoms, preferably from about 12 to about 16 or 18; X is from about  $\frac{1}{2}$  to about 20 on average, preferably from about 1 to about 10, more preferably from about 2 to about 6; and M is a water-soluble compatible cation such as those disclosed hereinabove. The alkylpolyethoxylate sulfates useful in the subject invention are typically condensation products of ethylene oxide and monohydric alcohols having from about 10 to about 20 carbon atoms. The alcohols can be derived from natural fats, e.g., coconut oil or tallow, or can be synthetic. Preferred cations of such surfactants are potassium, and especially sodium. Specific examples of alkylpolyethoxylate sulfates include sodium coconut alkylpolyethoxylate (3) ether sulfate, sodium  $\text{C}_{12-15}$  alkylpolyethoxylate (3) ether sulfate, sodium tallow alkylpolyethoxylate (6) ether sulfate, and potassium  $\text{C}_{12-13}$  alkylpolyethoxylate (1) ether sulfate.

Anionic surfactants include water-soluble salts of the higher fatty acids, or "soaps". This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, preferably from about 12 to about 18 carbon atoms.

Other anionic surfactants useful in the subject invention compositions include sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of alkylphenol ethylene oxide ether sulfates containing from about 1 to about 12 units of ethylene oxide per molecule, and wherein the alkyl group contains from about 8 to about 12 carbon atoms; and secondary alcohol sulfates containing from about 14 to about 18 carbon atoms.

Other anionic surfactants useful in the subject invention compositions include the water-soluble salts of esters of  $\alpha$ -sulfonated fatty acids containing from about 8 to about 20 carbon atoms in the fatty acid group and from about 1 to about 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-1-sulfonic acids containing from about 2 to about 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin and paraffin sulfonates containing from about 10 to about 20 carbon atoms;  $\beta$ -alkoxyalkane sulfonates containing from about 1 to about 3 carbon atoms in the alkyl group and from 8 to about 20 carbon atoms in the alkane moiety; alkylphenol polyethylene oxide ether sulfates, with from about 1 to about 10 units of ethylene

oxide per molecule on the average, in which the alkyl radicals contain from about 8 to about 12 carbon atoms; the reaction products of fatty acids esterified with isethionic acid, where fatty acids are derived from synthetic or natural sources; fatty acid amides of a methyl tauride in which the fatty acids are derived from synthetic or natural sources; and  $\beta$ -acetoxy- or  $\beta$ -acetamido-alkane sulfonates, where the alkane has from about 8 to about 22 carbon atoms.

#### **Solid Materials**

The subject dry particulate compositions necessarily comprise sufficient solid materials for the compositions to be in their dry particulate state. To achieve this the subject compositions comprise high levels of solid builders or solid fillers or mixtures thereof. Excluding the surfactants, perfume compositions, optional chlorine bleach material, and moisture discussed herein, the remainder of the subject compositions preferably comprises at least about 80%, more preferably from about 90% to about 100%, more preferably still from about 95% to about 99%, materials selected from such builders and fillers.

#### **Builders**

The compositions herein also preferably comprise at least about 1% phosphorus-containing builder, also preferably from about 2% to about 40%, more preferably from about 3% to about 20%, more preferably still from about 5% to about 12%.

Preferred phosphorus-containing builder materials are inorganic phosphate, pyrophosphate, or polyphosphate materials which have the ability to remove metal ions other than alkali metal ions from wash solutions by sequestration, including by chelation or by precipitation reactions. Preferred phosphorus-containing builders include trisodium phosphate, tetrasodium pyrophosphate, sodium tripolyphosphate, and sodium hexametaphosphate; sodium tripolyphosphate is the most preferred phosphorous-containing builder.

The compositions of the present invention also preferably comprise from about 1% to about 20% silicate builder, also preferably from about 3% to about 17%, more preferably from about 5% to about 15%.

The silicate builder materials are water-soluble silicates which are a mixture of  $\text{SiO}_2$  and  $\text{M}_2\text{O}$  ( $\text{M}=\text{Na}$  or  $\text{K}$ ), having a ratio of  $\text{SiO}_2:\text{M}_2\text{O}$  of from about 1:1 to about 3.6:1, preferably from about 1.6:1 to about 3.2:1. Such silicates help provide the desired alkalinity for the products herein during use.

#### **Blooming Perfume Composition**

The detergent compositions herein also comprise from about 0.05% to 3% of a blooming perfume composition. More preferably, the blooming perfume composition comprises from about 0.1% to 2% of the detergent compositions herein,

even more preferably from about 0.2% to 1.2%. Most preferably, the detergent compositions herein contain from about 0.4% to 0.8% of the blooming perfume composition.

A blooming perfume composition is one which comprises blooming perfume ingredients. A blooming perfume ingredient is characterized by its boiling point (B.P.) and its octanol/water partition coefficient (P). The octanol/water partition coefficient of a perfume ingredient is the ratio between its equilibrium concentrations in octanol and in water. The preferred perfume ingredients of this invention have a B.P., determined at the normal, standard pressure of about 760 mm Hg, of about 260°C or lower, preferably less than about 255°C; and more preferably less than about 250°C, and an octanol/water partition coefficient P of about 1,000 or higher. Since the partition coefficients of the preferred perfume ingredients of this invention have high values, they are more conveniently given in the form of their logarithm to the base 10, logP. Thus the preferred perfume ingredients of this invention have logP of about 3 or higher, preferably more than about 3.1, and even more preferably more than about 3.2.

The boiling points of many perfume ingredients are given in, e.g., "Perfume and Flavor Chemicals (Aroma Chemicals)," Steffen Arctander, published by the author, 1969, incorporated herein by reference.

The logP of many perfume ingredients has been reported; for example, the Pomona92 database, available from Daylight Chemical Information Systems, Inc. (Daylight CIS), Irvine, California, contains many, along with citations to the original literature. However, the logP values are most conveniently calculated by the "CLOGP" program, also available from Daylight CIS. This program also lists experimental logP values when they are available in the Pomona92 database. The "calculated logP" (ClogP) is determined by the fragment approach of Hansch and Leo (cf., A. Leo, in Comprehensive Medicinal Chemistry, Vol. 4, C. Hansch, P. G. Sammens, J. B. Taylor and C. A. Ramsden, Eds., p. 295, Pergamon Press, 1990, incorporated herein by reference). The fragment approach is based on the chemical structure of each perfume ingredient, and takes into account the numbers and types of atoms, the atom connectivity, and chemical bonding. The ClogP values, which are the most reliable and widely used estimates for this physicochemical property, are preferably used instead of the experimental logP values in the selection of perfume ingredients which are useful in the present invention.

Thus, when a perfume composition which is composed of ingredients having a B.P. of about 260°C or lower and a ClogP, or an experimental logP, of about 3 or higher, is used in a hand dish particulate cleaning composition, the perfume is very effusive and very noticeable when the product is used.

Table 1 gives some non-limiting examples of blooming perfume ingredients, useful in hand dish particulate cleaning compositions of the present invention. The blooming perfume compositions used in the present invention contain at least 5 different blooming perfume ingredients, preferably at least 6 different blooming perfume ingredients, more preferably at least 7 different blooming perfume ingredients, and even more preferably at least 8 different blooming perfume ingredients. Most common perfume ingredients which are derived from natural sources are composed of a multitude of components. For example, orange terpenes contain about 90% to about 95% d-limonene, but also contain many other minor ingredients. When each such material is used in the formulation of blooming perfume compositions of the present invention, it is counted as one single ingredient, for the purpose of defining the invention. Furthermore, the blooming perfume compositions of the present invention contain at least about 50 wt.% of blooming perfume ingredients, preferably at least about 55 wt.% of blooming perfume ingredients, more preferably at least about 60 wt.% of blooming perfume ingredients, and even more preferably at least about 70 wt.% of blooming perfume ingredients. The blooming perfume compositions herein should not contain any single ingredient at a level of more than about 60 %, by weight of the composition, preferably not more than about 50 %, by weight of the composition, and even more preferably not more than about 40 %, by weight of the composition.

Some of the blooming perfume ingredients used in the present invention can optionally be replaced by "delayed blooming" perfume ingredients. The optional delayed blooming perfume ingredients of this invention have a B.P., measured at the normal, standard pressure, of about 260°C or lower, preferably less than about 255°C; and more preferably less than about 250°C, and a logP or ClogP of less than about 3. Thus, when a perfume composition is composed of some preferred blooming ingredients and some delayed blooming ingredients, the perfume effect is longer lasting when the product is used. Table 2 gives some non-limiting examples of optional delayed blooming perfume ingredients, useful in the hand dish particulate cleaning compositions of the present invention. Delayed blooming perfume ingredients are used primarily in applications where the water will evaporate, thus liberating the perfume.

When delayed blooming perfume ingredients are used in combination with the blooming perfume ingredients in the blooming perfume compositions employed in the present invention, the weight ratio of blooming perfume ingredients to delayed blooming perfume ingredients is typically at least about 1, preferably at least about 1.3, more preferably about 1.5, and even more preferably about 2. The blooming perfume compositions contain at least about 50 wt.% of the combined



blooming perfume ingredients and delayed blooming perfume ingredients, preferably at least about 55 wt.% of the combined perfume ingredients, more preferably at least about 60 wt.% of the combined perfume ingredients, and even more preferably at least about 70 wt.% of the combined perfume ingredients. When some optional delayed blooming perfume ingredients are used in combination with the blooming perfume ingredients in the blooming perfume compositions, the blooming perfume compositions of the present invention contain at least 4 different blooming perfume ingredients and 2 different delayed blooming perfume ingredients, preferably at least 5 different blooming perfume ingredients and 3 different delayed blooming perfume ingredients, and more preferably at least 6 different blooming perfume ingredients and 4 different delayed blooming perfume ingredients.

In the perfume art, some auxiliary materials having no odor, or a low odor, are used, e.g., as solvents, diluents, extenders or fixatives. Non-limiting examples of these materials are ethyl alcohol, carbitol, diethylene glycol, dipropylene glycol, diethyl phthalate, triethyl citrate, isopropyl myristate, and benzyl benzoate. These materials are used for, e.g., solubilizing or diluting some solid or viscous perfume ingredients to, e.g., improve handling and/or formulating. These materials are useful in the blooming perfume compositions, but are not counted in the calculation of the limits for the definition/formulation of the blooming perfume compositions of the present invention.

Non-blooming perfume ingredients, which should be minimized in hand dish particulate cleaning compositions of the present invention, are those having a B.P. of more than about 260°C. Table 3 gives some non-limiting examples of non-blooming perfume ingredients. In some particular hand dish particulate cleaning compositions, some non-blooming perfume ingredients can be used in small amounts, e.g., to improve product odor.

It can be desirable to use blooming and delayed blooming perfume ingredients and even other ingredients, preferably in small amounts, in the blooming perfume compositions of the present invention, that have low odor detection threshold values. The odor detection threshold of an odorous material is the lowest vapor concentration of that material which can be detected. The odor detection threshold and some odor detection threshold values are discussed in, e.g., "Standardized Human Olfactory Thresholds", M. Devos et al. IRL Press at Oxford University Press, 1990, and "Compilation of Odor and Taste Threshold Values Data", F. A. Fazzalari, editor, ASTM Data Series DS 48A, American Society for Testing and Materials, 1978, both of said publications being incorporated by reference. The use of small amounts of non-blooming perfume ingredients that have

low odor detection threshold values can improve perfume odor character, without the potential negatives normally associated with such ingredients, e.g., spotting and/or filming on, e.g., dish surfaces. Non-limiting examples of perfume ingredients that have low odor detection threshold values useful in the present invention include coumarin, vanillin, ethyl vanillin, methyl dihydro isojasmonate, 3-hexenyl salicylate, isoeugenol, lylal, gamma-undecalactone, gamma-dodecalactone, methyl beta naphthyl ketone, and mixtures thereof. These materials are preferably present at low levels in addition to the blooming and delayed blooming ingredients, typically less than about 5%, preferably less than about 3%, more preferably less than about 2%, by weight of the blooming perfume compositions of the present invention.

**Table 1**  
**Examples of "Blooming" Perfume Ingredients**

<b>Perfume Ingredients</b>	<b>Approx. BP (°C)</b>	<b>Approx. ClogP</b>
allo-Ocimene	192	4.362
Allyl Heptoate	210	3.301
Anethol	236	3.314
Benzyl Butyrate	240	3.698
Camphene	159	4.192
Carvacrol	238	3.401
beta-Caryophyllene	256	6.333
cis-3-Hexenyl Tiglate	101	3.700
Citral (Neral)	228	3.120
Citronellol	225	3.193
Citronellyl Acetate	229	3.670
Citronellyl Isobutyrate	249	4.937
Citronellyl Nitrile	225	3.094
Citronellyl Propionate	242	4.628
Cyclohexyl Ethyl Acetate	187	3.321
Decyl Aldehyde	209	4.008
Dihydro Myrcenol	208	3.030
Dihydromyrcenyl Acetate	225	3.879
Dimethyl Octanol	213	3.737
Diphenyl Oxide	252	4.240
Dodecalactone	258	4.359
Ethyl Methyl Phenyl Glycidate	260	3.165
Fenchyl Acetate	220	3.485

gamma Methyl Ionone	230	4.089
gamma-n-Methyl Ionone	252	4.309
gamma-Nonalactone	243	3.140
Geranyl Acetate	245	3.715
Geranyl Formate	216	3.269
Geranyl Isobutyrate	245	4.393
Geranyl Nitrile	222	3.139
Hexenyl Isobutyrate	182	3.181
Hexyl Neopentanoate	224	4.374
Hexyl Tiglate	231	3.800
alpha-Ionone	237	3.381
beta-Ionone	239	3.960
gamma-Ionone	240	3.780
alpha-Irone	250	3.820
Isobornyl Acetate	227	3.485
Isobutyl Benzoate	242	3.028
Isononyl Acetate	200	3.984
Isononyl Alcohol	194	3.078
Isobutyl Quinoline	252	4.193
Isomenthol	219	3.030
para-Isopropyl Phenylacetaldehyde	243	3.211
Isopulegol	212	3.330
Lauric Aldehyde (Dodecanal)	249	5.066
Lilial (p-t-Bucinal)	258	3.858
d-Limonene	177	4.232
Linalyl Acetate	220	3.500
Menthyl Acetate	227	3.210
Methyl Chavicol	216	3.074
alpha-iso "gamma" Methyl Ionone	230	4.209
Methyl Nonyl Acetaldehyde	232	4.846
Methyl Octyl Acetaldehyde	228	4.317
Myrcene	167	4.272
Neral	228	3.120
Neryl Acetate	231	3.555
Nonyl Acetate	212	4.374
Nonyl Aldehyde	212	3.479
Octyl Aldehyde	223	3.845
Orange Terpenes (d-Limonene)	177	4.232

para-Cymene	179	4.068
Phenyl Heptanol	261	3.478
Phenyl Hexanol	258	3.299
alpha-Pinene	157	4.122
beta-Pinene	166	4.182
alpha-Terpinene	176	4.412
gamma-Terpinene	183	4.232
Terpinolene	184	4.232
Terpinyl acetate	220	3.475
Tetrahydro Linalool	191	3.517
Tetrahydro Myrcenol	208	3.517
Tonalid	246	6.247
Undecenal	223	4.053
Veratrol	206	3.140
Verdox	221	4.059
Vertenex	232	4.060

**Table 2**

**Examples of "Delayed Blooming" Perfume Ingredients**

<u>Perfume Ingredients</u>	<u>Approx BP (°C)</u>	<u>Approx. ClogP</u>
Allyl Caproate	185	2.772
Amyl Acetate	142	2.258
Amyl Propionate	161	2.657
Anisic Aldehyde	248	1.779
Anisole	154	2.061
Benzaldehyde	179	1.480
Benzyl Acetate	215	1.960
Benzyl Acetone	235	1.739
Benzyl Alcohol	205	1.100
Benzyl Formate	202	1.414
Benzyl Iso Valerate	246	2.887
Benzyl Propionate	222	2.489
Beta Gamma Hexenol	157	1.337
Camphor Gum	208	2.117
laevo-Carveol	227	2.265
d-Carvone	231	2.010
laevo-Carvone	230	2.203
Cinnamic Alcohol	258	1.950

Cinnamyl Formate	250	1.908
cis-Jasmone	248	2.712
cis-3-Hexenyl Acetate	169	2.243
Cuminic alcohol	248	2.531
Cuminic aldehyde	236	2.780
Cyclal C	180	2.301
Dimethyl Benzyl Carbinol	215	1.891
Dimethyl Benzyl Carbonyl Acetate	250	2.797
Ethyl Acetate	77	0.730
Ethyl Aceto Acetate	181	0.333
Ethyl Amyl Ketone	167	2.307
Ethyl Benzoate	212	2.640
Ethyl Butyrate	121	1.729
Ethyl Hexyl Ketone	190	2.916
Ethyl Phenyl Acetate	229	2.489
Eucalyptol	176	2.756
Eugenol	253	2.307
Fenchyl Alcohol	200	2.579
Flor Acetate (tricyclo Decenyl Acetate)	175	2.357
Frutene (tricyclo Decenyl Propionate)	200	2.260
Geraniol	230	2.649
Hexenol	159	1.397
Hexenyl Acetate	168	2.343
Hexyl Acetate	172	2.787
Hexyl Formate	155	2.381
Hydratropic Alcohol	219	1.582
Hydroxycitronellal	241	1.541
Indole	254	2.132
Isoamyl Alcohol	132	1.222
Isomenthone	210	2.831
Isopulegyl Acetate	239	2.100
Isoquinoline	243	2.080
Ligustral	177	2.301
Linalool	198	2.429
Linalool Oxide	188	1.575
Linalyl Formate	202	2.929
Menthone	207	2.650
Methyl Acetophenone	228	2.080

Methyl Amyl Ketone	152	1.848
Methyl Anthranilate	237	2.024
Methyl Benzoate	200	2.111
Methyl Benzyl Acetate	213	2.300
Methyl Eugenol	249	2.783
Methyl Heptenone	174	1.703
Methyl Heptine Carbonate	217	2.528
Methyl Heptyl Ketone	194	1.823
Methyl Hexyl Ketone	173	2.377
Methyl Phenyl Carbinyl Acetate	214	2.269
Methyl Salicylate	223	1.960
Methyl-N-Methyl Anthranilate	256	2.791
Nerol	227	2.649
Octalactone	230	2.203
Octyl Alcohol (Octanol-2)	179	2.719
para-Cresol	202	1.000
para-Cresyl Methyl Ether	176	2.560
para-Methoxy Acetophenone	260	1.801
para-Methyl Acetophenone	228	2.080
Phenoxy Ethanol	245	1.188
Phenyl Acetaldehyde	195	1.780
Phenyl Ethyl Acetate	232	2.129
Phenyl Ethyl Alcohol	220	1.183
Phenyl Ethyl Dimethyl Carbinol	238	2.420
Prenyl Acetate	155	1.684
Propyl Butyrate	143	2.210
Pulegone	224	2.350
Rose Oxide	182	2.896
Safrole	234	1.870
4-Terpinenol	212	2.749
alpha-Terpineol	219	2.569
Viridine	221	1.293

**Table 3**  
**Examples of Non-Blooming Perfume Ingredients**

<b><u>Perfume Ingredients</u></b>	<b><u>Appr ximate B.P. ( C )</u></b>	<b><u>Approx. ClogP</u></b>
Allyl Cyclohexane Propionate	267	3.935
Ambrettolide	300	6.261

Amyl Benzoate	262	3.417
Amyl Cinnamate	310	3.771
Amyl Cinnamic Aldehyde	285	4.324
Amyl Cinnamic Aldehyde Dimethyl Acetal	300	4.033
iso-Amyl Salicylate	277	4.601
Aurantiol	450	4.216
Benzophenone	306	3.120
Benzyl Salicylate	300	4.383
Cadinene	275	7.346
Cedrol	291	4.530
Cedryl Acetate	303	5.436
Cinnamyl Cinnamate	370	5.480
Coumarin	291	1.412
Cyclohexyl Salicylate	304	5.265
Cyclamen Aldehyde	270	3.680
Dihydro Isojasmonate	+300	3.009
Diphenyl Methane	262	4.059
Ethylene Brassylate	332	4.554
Ethyl Methyl Phenyl Glycidate	260	3.165
Ethyl Undecylenate	264	4.888
iso-Eugenol	266	2.547
Exaltolide	280	5.346
Galaxolide	+260	5.482
Geranyl Anthranilate	312	4.216
Hexadecanolide	294	6.805
Hexenyl Salicylate	271	4.716
Hexyl Cinnamic Aldehyde	305	5.473
Hexyl Salicylate	290	5.260
Linalyl Benzoate	263	5.233
2-Methoxy Naphthalene	274	3.235
Methyl Cinnamate	263	2.620
Methyl Dihydrojasmonate	+300	2.275
beta-Methyl Naphthyl ketone	300	2.275
Musk Indanone	+250	5.458
Musk Ketone	MP = 137°C	3.014
Musk Tibetine	MP = 136°C	3.831
Myristicin	276	3.200
delta-Nonalactone	280	2.760

Oxahexadecanolide-10		+300	4.336
Oxahexadecanolide-11		MP = 35°C	4.336
Patchouli Alcohol	285	4.530	
Phantolide	288	5.977	
Phenyl Ethyl Benzoate		300	4.058
Phenylethylphenylacetate	325	3.767	
alpha-Santalol	301	3.800	
Thibetolide	280	6.246	
delta-Undecalactone	290	3.830	
gamma-Undecalactone		297	4.140
Vanillin		285	1.580
Vetiveryl Acetate	285	4.882	
Yara-Yara	274	3.235	

(a) M.P. is melting point: these ingredients have a B.P. higher than about 260°C.

The perfumes suitable for use in the hand dish particulate cleaning compositions herein can be formulated from known fragrance ingredients and for purposes of enhancing environmental compatibility, the perfume compositions used herein are preferably substantially free of halogenated fragrance materials and nitromusks.

The blooming perfume compositions hereinbefore described are preferably incorporated into moisture-activated, complexed or encapsulated perfume particles for use in the particulate hand dish cleaning compositions of this invention. Such perfume particles include, for example, cyclodextrin/perfume inclusion complexes, polysaccharide cellular matrix perfume microcapsules, and the like. Encapsulation of the blooming perfume compositions minimizes the depletion of the volatile blooming perfume ingredients when the product box is opened and during storage. Perfume is released when products are dissolved in washing solution to thereby provide a pleasant odor signal in use. Furthermore, the water-activated perfume carrier protects the perfume from chemical degradation caused by the different bleach systems which are commonly present in the particulate hand dishwashing detergent compositions of this invention.

It is also preferable to use both free perfume and encapsulated perfume in the same particulate hand dishwashing detergent composition, with the two perfumes being either the same, or two different perfumes. Normally, the free perfume mainly provides the product (or box) perfume odor, and covers any base product odor, while the encapsulated perfume mainly provides the in-use perfume odor when the detergent composition is diluted into the wash water.



Due to the minimized loss of the volatile ingredients of the blooming perfume compositions as a result of encapsulating said compositions in the water-activated protective perfume carriers, the blooming perfume compositions which are used in the encapsulated form can contain less blooming perfume ingredients than those used in the free, unencapsulated form. The encapsulated and/or complexed blooming perfume compositions can typically contain at least about 20%, preferably at least about 30%, and more preferably at least 40%, of blooming perfume ingredients. Higher levels of blooming perfume ingredients and delayed blooming perfume ingredients are also preferred.

Especially preferred perfume particulates comprise cyclodextrin inclusion complexes of the blooming perfume compositions herein with a particle size of less than about 12 microns. As used herein, the term "cyclodextrin" includes any of the known cyclodextrins such as unsubstituted cyclodextrins containing from six to twelve glucose units, especially, alpha-, beta-, and gamma-cyclodextrins, and/or their derivatives, and/or mixtures thereof. The alpha-cyclodextrin consists of 6, the beta-cyclodextrin 7, and the gamma-cyclodextrin 8, glucose units arranged in a donut-shaped ring. The specific coupling and conformation of the glucose units give the cyclodextrins a rigid, conical molecular structure with a hollow interior of a specific volume. The "lining" of the internal cavity is formed by hydrogen atoms and glycosidic bridging oxygen atoms, therefore this surface is fairly hydrophobic. These cavities can be filled with all or a portion of an organic molecule with suitable size to form an "inclusion complex." Alpha-, beta-, and gamma-cyclodextrins can be obtained from, among others, American Maize-Products Company (Amaizo), Hammond, Indiana.

Cyclodextrin derivatives are disclosed in U.S. Pat. Nos: 3,426,011, Parmerter et al., issued Feb. 4, 1969; 3,453,257, 3,453,258, 3,453,259, and 3,453,260, all in the names of Parmerter et al., and all also issued July 1, 1969; 3,459,731, Gramera et al., issued Aug. 5, 1969; 3,553,191, Parmerter et al., issued Jan. 5, 1971; 3,565,887, Parmerter et al., issued Feb. 23, 1971; 4,535,152, Szejtli et al., issued Aug. 13, 1985; 4,616,008, Hirai et al., issued Oct. 7, 1986; 4,638,058, Brandt et al., issued Jan. 20, 1987; 4,746,734, Tsuchiyama et al., issued May 24, 1988; and 4,678,598, Ogino et al., issued Jul. 7, 1987, all of said patents being incorporated herein by reference. Examples of cyclodextrin derivatives suitable for use herein are methyl-beta-cyclodextrin, hydroxyethyl-beta-cyclodextrin, and hydroxypropyl-beta-cyclodextrin of different degrees of substitution (D.S.), available from Amaizo; Wacker Chemicals (USA), Inc.; and Aldrich Chemical Company. Water-soluble derivatives are also highly desirable.

The individual cyclodextrins can also be linked together, e.g., using multifunctional agents to form oligomers, polymers, etc. Examples of such materials are available commercially from Amaizo and from Aldrich Chemical Company (beta-cyclodextrin/epichlorohydrin copolymers). The preferred cyclodextrin for use in forming the perfume inclusion complexes is beta-cyclodextrin. It is also desirable to use mixtures of cyclodextrins. Preferably at least a major portion of the cyclodextrins are alpha-, beta- and/or gamma-cyclodextrins, more preferably alpha- and beta-cyclodextrins. Some cyclodextrin mixtures are commercially available from, e.g., Ensuiko Sugar Refining Company, Yokohama, Japan.

The cyclodextrin/perfume inclusion complexes useful herein are formed in any of the ways known in the art. Typically, the complexes are formed either by bringing the blooming perfume composition and the cyclodextrin together in a suitable solvent, e.g., water, or, preferably, by kneading/slurrying the ingredients together in the presence of a suitable, preferably minimal, amount of solvent, preferably water. The kneading/slurrying method is particularly desirable because it produces smaller complex particles and requires the use of less solvent, eliminating or reducing the need to further reduce particle size and separate excess solvent. Disclosures of complex formation can be found in Atwood, J.L., J.E.D. Davies & D.D. MacNichol, (Ed.): Inclusion Compounds, Vol. III, Academic Press (1984), especially Chapter 11, Atwood, J.L. and J.E.D. Davies (Ed.): Proceedings of the Second International Symposium of Cyclodextrins Tokyo, Japan, (July, 1984), and J. Szejtli, Cyclodextrin Technology, Kluwer Academic Publishers (1988), said publications incorporated herein by reference.

In general, perfume/cyclodextrin complexes have a molar ratio of perfume ingredients to cyclodextrin of about 1:1. However, the molar ratio can be either higher or lower, depending on the size of the perfume molecules and the identity of the cyclodextrin compound. The molar ratio can be determined by forming a saturated solution of the cyclodextrin and adding the perfume to form the complex. In general the complex will precipitate readily. If not, the complex can usually be precipitated by the addition of electrolyte, change of pH, cooling, etc. The complex can then be analyzed to determine the ratio of perfume to cyclodextrin.

As stated hereinbefore, the actual complexes are determined by the size of the cavity in the cyclodextrin and the size of the perfume molecules. Desirable complexes can be formed using mixtures of cyclodextrins since the blooming perfumes are mixtures of materials that vary widely in size. It is usually desirable that at least a majority of the material be alpha-, beta-, and/or gamma-cyclodextrin, more preferably beta-cyclodextrin. The content of the perfume in the beta-

cyclodextrin complex is typically from about 5% to about 15%, more normally from about 8% to about 13%. The particulate hand dishwashing detergent compositions of this invention preferably will comprise of from 0% to about 15%, preferably from about 1% to about 10%, more preferably from about 2% to about 8% of cyclodextrin/perfume complex.

Continuous complexation operation usually involves the use of supersaturated solutions, kneading/slurrying method, and/or temperature manipulation, e.g., heating and then either cooling, freeze-drying, etc. The complexes are dried to a dry powder to make the desired composition. In general, the fewest possible process steps are preferred to avoid loss of perfume.

Cyclodextrin/perfume complexes used in this invention having a particle size of less than about 12 microns, preferably less than about 10 microns, more preferably less than about 8 microns, and even more preferably less than about 5 microns, improve the release, especially the speed of release of the perfume when the complexes are wetted.

The particle size is typically between about 0.001 and 10 microns, preferably between about 0.05 and 5 microns. It is highly desirable that at least an effective amount of the blooming perfume be in complexes having the said particle sizes. It is desirable that at least about 75%, preferably at least about 80%, more preferably at least about 90%, and even more preferably at least about 100%, of the complex that is present have these particle sizes.

These small particles of the invention are conveniently prepared by kneading methods and/or grinding techniques. Cyclodextrin complexes with large particle sizes can be pulverized to obtain the desired smaller particles of less than about 12 microns by using, e.g., a fluid energy mill. Examples of fluid energy mills are the Trost Air Impact Pulverizers, sold by Garlock Inc., Plastomer Products, Newtown, Pennsylvania; the Micronizer fluid energy mills sold by Sturtevant, Inc., Boston, Massachusetts; and the Spiral Jet Mill sold by Alpine Division, MicroPul Corporation (Hosokawa Micron International, Inc.), Summit, New Jersey.

As used herein, the particle size refers to the largest dimension of the particle and to the ultimate (or primary) particles. The size of these primary particles can be directly determined with optical or scanning electron microscopes. The slides must be carefully prepared so that each contains a representative sample of the bulk cyclodextrin complexes. The particles sizes can also be measured by any of the other well-known methods, e.g., wet sieving (non-aqueous), sedimentation, light scattering, etc. A convenient instrument that can be used to determine the particle size distribution of the dry complex powder directly (without having to make a liquid suspension or dispersion) is the Malvern Particle and Droplet Sizer, Model

2600C, sold by Malvern Instruments, Inc., Southborough, Massachusetts. Some caution should be observed in that some of the dry particles may remain agglomerated. The presence of agglomerates can be further determined by microscopic analysis. Some other suitable methods for particle size analysis are described in the article "Selecting a particle size analyzer: Factors to consider," by Michael Pohl, published in Powder and Bulk Engineering, Volume 4 (1990), pp. 26-29, incorporated herein by reference. It is recognized that the very small particles can readily aggregate to form loose agglomerates that are easily broken apart by either some mechanical action or by the action of water. Accordingly, particles should be measured after they are broken apart, e.g., by agitation or sonication. The method, of course, should be selected to accommodate the particle size and maintain the integrity of the complex particles, with iterative measurements being made if the original method selected proves to be inappropriate.

The blooming perfume compositions added to the detergent products herein as perfume particles may also be protected by incorporating them into matrix perfume microcapsules. Water-soluble cellular matrix perfume microcapsules are solid particles containing the blooming perfume ingredients stably held in the cells. The water-soluble matrix material comprises mainly polysaccharide and polyhydroxy compounds. The polysaccharides are preferably higher polysaccharides of the non-sweet, colloidally-soluble types, such as natural gums, e.g., gum arabic, starch derivatives, dextrinized and hydrolyzed starches, and the like. The polyhydroxy compounds are preferably alcohols, plant-type sugars, lactones, monoethers, and acetals. The cellular matrix microcapsules useful in the present invention are prepared by, e.g., (1) forming an aqueous phase of the polysaccharide and polyhydroxy compound in proper proportions, with added emulsifier if necessary or desirable; (2) emulsifying the blooming perfume compositions in the aqueous phase; and (3) removing moisture while the mass is plastic or flowable, e.g., by spray drying droplets of the emulsion. The matrix materials and process details are disclosed in, e.g., U.S. Pat. No. 3,971,852, Brenner et al., issued July 27, 1976, which is incorporated herein by reference.

Moisture-activated perfume microcapsules can be obtained commercially, e.g., as IN-CAP® from Polak's Frutal Works, Inc., Middletown, New York; and as Optilok System® encapsulated perfumes from Encapsulated Technology, Inc., Nyack, New York.

The particulate hand dishwashing detergent compositions of this invention will preferably comprise of from 0% to about 6%, preferably from about 0.2% to about 4%, more preferably from about 0.4% to about 2% of water-activated matrix perfume microcapsules. Water-soluble matrix perfume microcapsules preferably

have size of from about 0.5 micron to about 300 microns, more preferably from about 1 micron to about 200 microns, most preferably from about 2 microns to about 100 microns.

### **Optional Ingredients**

Optional ingredients which may be incorporated in the particulate hand dish cleaning compositions of the present invention include, but are not limited to, the following:

The detergent compositions of the present invention may optionally contain a chlorine bleach material which provides from about 0.003% to about 4% available chlorine based on the weight of the composition, preferably from about 0.01% to about 2%, more preferably from about 0.05% to about 1%, more preferably still from about 0.1% to about 0.5%.

Methods for determining "available chlorine" of compositions incorporating chlorine bleach materials are well known in the art. Available chlorine is the chlorine which can be liberated by acidification of an aqueous solution of hypochlorite ions (or a material that can form hypochlorite ions in aqueous solution) and at least a molar equivalent amount of chloride ions. Numerous materials are known which provide available chlorine.

A conventional analytical method for determining available chlorine is by addition of an excess of an iodide salt and titration of the liberated free iodine with a reducing agent, such as sodium thiosulfate. Samples of the detergent compositions are typically dissolved in a water-chloroform mixture to extract any interfering organics. prior to analyzing for available chlorine. An aqueous solution containing about 1% of the subject composition is used to determine available chlorine of the composition.

Many chlorine bleach materials are known, such as disclosed in Mizuno, W.G., "Dishwashing", Detergency: Theory and Test Methods, Surfactant Science Series, Volume 5, Part III, pages 872-878. Chlorine bleach materials useful in the subject invention compositions include alkali metal hypochlorites, hypochlorite addition products, and N-chloro compounds usually containing an organic radical. N-chloro compounds are usually characterized by a double bond on the atom adjacent to a trivalent nitrogen and a chlorine ( $\text{Cl}^+$ ) attached to the nitrogen which is readily exchanges with  $\text{H}^+$  or  $\text{M}^+$  (where  $\text{M}^+$  is a common metal ion such as  $\text{Na}^+$ ,  $\text{K}^+$ , etc.), so as to release  $\text{HOCl}$  or  $\text{OCl}^-$  on hydrolysis.

Preferred alkali metal hypochlorite compounds useful in the detergent compositions herein include sodium hypochlorite, potassium hypochlorite, and lithium hypochlorite. Although known as chlorine bleach materials, alkaline earth metal hypochlorites, such as calcium hypochlorite and magnesium hypochlorite, are

not preferred for the present compositions due to poor compatibility of the alkaline earth metal cations with the anionic surfactants.

A preferred hypochlorite addition product useful in the detergent compositions of this invention is chlorinated trisodium phosphate which is a crystalline hydrated double salt of trisodium phosphate and sodium hypochlorite, which is prepared by crystallizing from an aqueous blend of sodium hypochlorite, caustic soda, trisodium phosphate, and disodium phosphate. Chlorinated trisodium phosphate is typically commercially available as chlorinated trisodium phosphate dodecahydrate.

Examples of N-chloro compounds useful as chlorine bleach materials in the subject compositions include trichloroisocyanuric acid, dichloroisocyanuric acid, monochloroisocyanuric acid, 1,3-dichloro-5,5-dimethylhydantoin, 1-chloro-5,5-dimethylhydantoin, N-chlorosuccinimide, N-chlorosulfamate, N-chloro-p-nitroacetanilide, N-chloro-o-nitroacetanilide, N-chloro-m-nitroacetanilide, N-m-dichloroacetanilide, N-p-dichloroacetanilide, Dichloramine-T, N-chloro-propionanilide, N-chlorobutyranilide, N-chloroacetanilide, N-o-dichloroacetanilide, N-chloro-p-acetotoluide, N-chloro-m-acetotoluide, N-chloroformanilide, N-chloro-o-acetotoluide, Chloramine-T, ammonia monochloramine, albuminoid chloramines, N-chlorosulfamide, Chloramine B, Dichloramine B, Di-Halo (bromochlorodimethylhydantoin), N,N'-dichlorobenzoylene urea, p-toluene sulfodichloroamide, trichloromelamine, N-chloroammeline, N,N'-dichloroazodicarbonamide, N-chloroacetyl urea, N,N'-dichlorobiuret, chlorinated dicyandiamide, and alkali metal salts of the above acids, and stable hydrates of the above compounds.

Particularly preferred chlorine bleach materials useful in the detergent compositions herein are chloroisocyanuric acids and alkali metal salts thereof, preferably potassium, and especially sodium salts thereof. Examples of such compounds include trichloroisocyanuric acid, dichloroisocyanuric acid, sodium dichloroisocyanurate, potassium dichloroisocyanurate, and trichloro-potassium dichloroisocyanurate complex. The most preferred chlorine bleach material is sodium dichloroisocyanurate; the dihydrate of this material is particularly preferred due to its excellent stability.

The compositions of the present invention may also comprise, as an optional builder, from 0% to about 30% alkali metal carbonate, preferably sodium carbonate, preferably from about 5% to about 20%.

The compositions of the present invention may also comprise from 0% to about 98 % filler materials such as sodium sulfate, sodium chloride, sucrose, sucrose esters, etc., preferably from about 5% to about 75%, also preferably from about 10%

to about 60%, more preferably from about 20% to about 50%. The preferred filler material is sodium sulfate.

The compositions of the present invention may also comprise from 0% to about 2% antiredeposition materials such as carboxymethylcellulose, polyethyleneglycol, polyvinylpyrrolidone, polyvinylalchols, etc., preferably from about 0.5% to about 1%. Carboxymethylcellulose is the preferred antiredeposition material.

The compositions of the present invention may also comprise from 0% to about 5% minor ingredients including, but not limited to, brighteners, dyes, etc., preferably from about 0.5% to about 2%.

The compositions of the subject invention comprise from 0% to about 10% moisture, preferably from about 1% to about 8%, more preferably from about 3% to about 7%.

#### **Process for Preparation/Method of Use**

The dry particulate compositions of the present invention can be made by a variety of processes, including dry blending of particulate ingredients and addition of liquid ingredients by spraying on and blending in. Preferred processes for making the detergent compositions herein are well-known processes for making spray-dried detergent products. Typically, surfactant is blended with builders, filler materials, other non-volatile and non-heat sensitive components, and sufficient water to form a slurry which is spray-dried using a standard tower operation. To the dry particulate product thus produced is added the chlorine bleach material and minors via dry blending, spray on, or a combination thereof.

Other preferred processes for making the detergent compositions herein are processes for making agglomerated materials in various mixers. Suitable mixers include high-speed, high-shear mixers such as the Loedige CB®, the Shugi Granulator®, and the Drais K-TTP®, and moderate-speed mixers including plowshare mixers, such as the Loedige KM® and the Drais K-T®. The dry components of the subject compositions are fed to such mixers and intimately mixed. Liquid components can be sprayed into such mixers and be mixed with the dry components therein, or can be sprayed on the mixtures after discharge from the mixer, preferably with an additional blending step.

The present invention also involves methods of cleaning cooking or eating utensils by washing them by hand in an aqueous solution or dispersion of cleaning compositions of the type herein described. In fact, for the hand dishwashing methods herein, the washing solution can be formed from a composition containing only 1% of an anionic surfactant and from about 0.005% to 3% of one or more blooming perfume ingredients. Preferred solutions or dispersions of the

compositions herein for cleaning cooking or eating utensils are aqueous-based comprising from about 1% to about 8%, preferably from about 2% to about 6%, of the compositions hereinbefore described, and the balance water.

### Examples

The following non-limiting examples exemplify perfume compositions, moisture-activated perfume particles and detergent compositions using such perfumes and perfume particles.

The following perfume compositions are prepared:

#### **PERFUME A - Citrus Floral Type**

<u>Perfume Ingredients</u>	<u>Wt. %</u>
<u>Blooming Ingredients</u>	
Citral	4
Citronellol	5
Citronellyl Nitrile	3
para Cymene	2
Decyl Aldehyde	1
Dihydro Myrcenol	15
Geranyl Nitrile	3
alpha-Ionone	2
Linalyl Acetate	5
gamma-Methyl Ionone	3
Myrcene	1.5
Orange Terpenes	15
beta-Pinene	3
<u>Delayed Blooming Ingredients</u>	
Anisic Aldehyde	1
beta gamma Hexenol	0.3
cis-3-Hexenyl Acetate	0.2
cis-Jasmone	1
Linalool	8
Nerol	3
alpha-Terpineol	4
<u>Other Ingredients</u>	
Amyl Salicylate	1
Hexyl Cinnamic Aldehyde	5
Hexyl Salicylate	3
P.T. Bucinal	5
Patchouli	1



Phenyl Hexanol	5
<b>Total</b>	<b>100</b>

**PERFUME B - Rose Floral Type**

<u><b>Perfume Ingredients</b></u>	<u><b>Wt. %</b></u>
<u><b>Blooming Ingredients</b></u>	
Citronellol	15
Citronellyl Nitrile	3
Decyl Aldehyde	1
Dihydro Myrcenol	5
Dimethyl Octanol	5
Diphenyl Oxide	1
Geranyl Acetate	3
Geranyl Formate	3
alpha-Ionone	3
Isobornyl Acetate	4
gamma-Methyl Ionone	4
P. T. Bucinal	10
<u><b>Delayed Blooming Ingredients</b></u>	
Geraniol	7
Phenyl Ethyl Alcohol	15
Terpineol	5
<u><b>Other Ingredients</b></u>	
Aurantiol	3
Benzophenone	3
Hexyl Cinnamic Aldehyde	10
<b>Total</b>	<b>100</b>

**PERFUME C - Natural Lime Type**

<u><b>Perfume Ingredients</b></u>	<u><b>Wt. %</b></u>
<u><b>Blooming Ingredients</b></u>	
Camphene	1
Caryophyllene	1
para-Cymene	1
Geranyl Acetate	2
d-Limonene	49
Myrcene	2
alpha-Pinene	1.5
beta-Pinene	2
Terpinolene	20

**Delayed Blooming Ingredients**

Eucalyptol	1.5
Fenchyl alcohol	1
Linalool	3
Terpinene-4-ol	2
Terpineol	10

**Other Ingredients**

Bisabolene	3
<b>Total</b>	<b>100</b>

**PERFUME D - Natural Lemon Type**

<b><u>Perfume Ingredients</u></b>	<b><u>Wt. %</u></b>
-----------------------------------	---------------------

**Blooming Ingredients**

Citral	4
Frutene	15
d-Limonene	50
Linalyl Acetate	6
alpha-Pinene	4
beta-Pinene	3

**Other Ingredients**

Methyl Dihydrojasmonate	18
<b>Total</b>	<b>100</b>

**PERFUME E - Fruity Lemon Type**

<b><u>Perfume Ingredients</u></b>	<b><u>Wt. %</u></b>
-----------------------------------	---------------------

**Blooming Ingredients**

Dihydro Myrcenol	1
Dihydro Terpineol	2.5
para-Cymene	0.5
Isononyl Alcohol	0.5
Tetrahydro Linalool	45
Tetrahydro Myrcenol	44
Verdox	1

**Delayed Blooming Ingredients**

Camphor gum	0.5
Dimethyl Benzyl Carbinol	1
Eucalyptol	1
Fenchyl Alcohol	1.5

**Other Ingredients**

Dimetol	1.5
<b>Total</b>	<b>100</b>

**PERFUME F - Citrus Lime Type**

<b><u>Perfume Ingredients</u></b>	<b><u>Wt. %</u></b>
-----------------------------------	---------------------

**Blooming Ingredients**

Citral	3
--------	---

Citronellyl Nitrile	2
Decyl Aldehyde	0.5
Dihydro Myrcinol	10
Frutene	5
Geranyl Nitrile	3
Linalyl Acetate	5
Octyl Aldehyde	0.5
Orange Terpenes	30
para-Cymene	1.5
Phenyl Hexanol	5
alpha-Pinene	2.5
Terpinyl Acetate	2
Tetrahydro Linalool	3
Verdox	1
<b><u>Delayed Blooming Ingredients</u></b>	
Benzyl Propionate	2
Eucalyptol	2
Fenchyl Alcohol	0.5
Flor Acetate	7
beta gamma Hexenol	0.5
Linalool	7
alpha-Terpineol	2
<b><u>Other Ingredients</u></b>	
Methyl Dihydro Jasmonate	5
<b>Total</b>	<b>100</b>

**PERFUME G - Fruity Lemon (Bleach Stable)**

<b><u>Perfume Ingredients</u></b>	<b><u>Wt. %</u></b>
<b><u>Blooming Ingredients</u></b>	
Dihydro Myrcenol	1
Dihydro Terpineol	2.5
para-Cymene	0.5
Isononyl Alcohol	0.5
Tetrahydro Linalool	45
Tetrahydro Myrcenol	44
Verdox	1
<b><u>Delayed Blooming Ingredients</u></b>	
Camphor gum	0.5
Dimethyl Benzyl Carbinol	1

Eucalyptol	1
Fenchyl Alcohol	1.5
<b><u>Other Ingredients</u></b>	
Dimetol	1.5
<b>Total</b>	<b>100</b>

Following are non-limiting examples of moisture-activated encapsulated perfumes, e.g., cyclodextrin/perfume inclusion complexes and matrix perfume microcapsules, that can be incorporated into the compositions of this invention.

**Cyclodextrin/Perfume Complex.**

A mobile slurry is prepared by mixing about 1 Kg of beta-cyclodextrin and about 1 liter of water in a stainless steel mixing bowl of a Kitchen Aid mixer using a plastic coated heavy-duty mixing blade. Mixing is continued while about 175 g of the perfume is slowly added. The liquid-like slurry immediately starts to thicken and becomes a creamy paste. Stirring is continued for about 30 minutes. About 0.5 liter of water is then added to the paste and blended well. Stirring is resumed for about an additional 30 minutes. During this time the complex again thickens, although not to the same degree as before the additional water is added. The resulting creamy complex is spread in a thin layer on a tray and allowed to air dry. This produces about 1.1 Kg of granular solid which is ground to a fine powder.

**Matrix Perfume Microcapsules.**

An example of water-activated matrix perfume microcapsules is made according to Example 1 of U.S. Pat No. 3,971,852, except that a blooming perfume composition is used instead of orange oil.

Using the blooming perfume compositions and/or encapsulated blooming perfume compositions, as described hereinbefore, the following dry particulate hand dish detergent compositions are prepared:

**Example 1**

<b>Ingredient</b>	<b>Weight Percent</b>
LAS	25
Sodium triphosphate	40
Sodium silicate (ratio 1.6)	7.5
Perfume A	1.2
Sodium sulfate	18
Carboxymethylcellulose	1
Moisture	balance

**Example 2**

<b>Ingredient</b>	<b>Weight Percent</b>
LAS	20
Sodium tripolyphosphate	15
Sodium silicate (ratio 2.0)	10
Perfume B	0.8
Sodium sulfate	30
Sodium carbonate	20
Moisture	balance

**Example 3**

<b>Ingredient</b>	<b>Weight Percent</b>
Coconut fatty alcohol sulfate	24
Sodium tripolyphosphate	20
Sodium silicate (ratio 1.6)	3
Chlorinated trisodium phosphate	5
Sodium carbonate	15
Sodium sulfate	28
Perfume G	0.8
Moisture	balance

**Example 4**

<b>Ingredient</b>	<b>Weight Percent</b>
LAS	28
Sodium tripolyphosphate	5
Sodium silicate (ratio 2.35)	14
Sodium dichloroisocyanurate dihydrate	0.5
Sodium sulfate	45
Perfume C	0.6
Moisture	balance

**Example 5**

<b>Ingredient</b>	<b>Weight Percent</b>
LAS	25
Sodium tripolyphosphate	10
Sodium silicate (ratio 2.0)	6
Sodium dichloroisocyanurate	0.3
Sodium sulfate	43

Sodium carbonate	10
Perfume G	0.7
Moisture	balance

**Example 6**

Ingredient	Weight Percent
ABS	18
Sodium tripolyphosphate	15
Sodium silicate (ratio 2.0)	8
Perfume D	1
Sodium carbonate	9
Sodium sulphate	45
Moisture	balance

**Example 7**

Ingredient	Weight Percent
ABS	18
Sodium tripolyphosphate	15
Sodium silicate (ratio 2.0)	8
Perfume E	1
Sodium carbonate	9
Sodium sulphate	45
Perfume G	0.8
Moisture	balance

**Example 8**

Ingredient	Weight Percent
LAS	24
Sodium triphosphate	38
Sodium silicate (ratio 1.6)	8
beta-Cyclodextrin/Perfume C complex powder	6
Sodium sulfate	17
Carboxymethylcellulose	1
Moisture	balance

**Example 9**

Ingredient	Weight Percent
LAS	20
Sodium tripolyphosphate	14
Sodium silicate (ratio 2.0)	10
Perfume A	0.4
beta-Cyclodextrin/Perfume C complex powder	4
Sodium sulfate	28
Sodium carbonate	19
Moisture	balance

**Example 10**

Ingredient	Weight Percent
Coconut fatty alcohol sulfate	23
Sodium tripolyphosphate	20
Sodium silicate (ratio 1.6)	3
Chlorinated trisodium phosphate	5
Sodium carbonate	14
Sodium sulfate	26
Perfume G	0.4
beta-Cyclodextrin/Perfume E complex powder	4
Moisture	balance

**Example 11**

Ingredient	Weight Percent
LAS	28
Sodium tripolyphosphate	5
Sodium silicate (ratio 2.35)	14
Sodium dichloroisocyanurate dihydrate	0.5
Sodium sulfate	45
beta-Cyclodextrin/Perfume F complex powder	6
Moisture	balance



**Example 12**

<b>Ingredient</b>	<b>Weight Percent</b>
LAS	25
Sodium tripolyphosphate	10
Sodium silicate (ratio 2.0)	6
Sodium dichloroisocyanurate	0.3
Sodium sulfate	42
Sodium carbonate	10
Matrix microcapsules of Perfume F	1.4
Moisture	balance

**Example 13**

<b>Ingredient</b>	<b>Weight Percent</b>
ABS	18
Sodium tripolyphosphate	15
Sodium silicate (ratio 2.0)	8
Perfume A	0.5
Matrix microcapsules of Perfume E	1
Sodium carbonate	9
Sodium sulphate	45
Moisture	balance

**Example 14**

<b>Ingredient</b>	<b>Weight Percent</b>
ABS	18
Sodium tripolyphosphate	15
Sodium silicate (ratio 2.0)	8
Perfume E	1
Sodium carbonate	9
Sodium sulphate	45
Perfume E	0.3
Matrix microcapsules of Perfume B	1.2
Moisture	balance

**Example 15**

<b>Ingredient</b>	<b>Weight Percent</b>
LAS	28
Sodium tripolyphosphate	5

Sodium silicate (ratio 1.6)	13.2
Perfume A	0.6
Sodium Sulfate	47.4
Moisture	5.5
Misc.	0.3

In the composition of Example 15, Perfume A can be replaced by Perfume C, Perfume F, or Perfume G.

While particular embodiments of the subject invention have been described, it would be obvious to those skilled in the art that various changes and modifications can be made without departing from the spirit and scope of the invention. It is intended to cover, in the appended claims, all such modifications that are within the scope of this invention.

CLAIMS:

1. A perfumed, dry particulate detergent composition useful for hand washing eating and cooking utensils, which composition comprises:
  - (a) at least 1%, preferably at least 18%, by weight of an anionic surfactant;
  - (b) from 0.5% to 3% by weight of a blooming perfume composition that contains at least five different blooming perfume ingredients, each of which ingredients has a boiling point of 260°C or lower and a calculated  $\log_{10}$  of its octanol/water partition coefficient, P, of 3 or higher, with the proviso that when said blooming perfume composition is present as part of a cyclodextrin/perfume complex, the particles of said complex are less than 12 microns in size;
  - (c) optionally a chlorine bleach material which provides from 0% to 4% available chlorine;
  - (d) from 0% to 10% moisture; and
  - (e) a remainder being all components of the composition other than (a) through (d), the remainder comprising at least 80%, preferably at least 90%, solid materials selected from builders, fillers, and mixtures thereof.
  
2. A perfumed, dry particulate detergent composition useful for hand washing eating and cooking utensils, which composition comprises:
  - (a) at least 1% by weight of an anionic surfactant;
  - (b) at least 1% by weight of a phosphorous-containing builder;
  - (c) from 1% to 20% by weight of a silicate builder; and
  - (d) from 0.5% to 3% by weight of a blooming perfume composition that contains at least five different blooming perfume ingredients, each of which ingredients has a boiling point of 260°C or lower and a calculated  $\log_{10}$  of its octanol/water partition coefficient, P, of 3 or higher, with the proviso that when said blooming perfume composition is present as part of a cyclodextrin/perfume complex, the particles of said complex are less than 12 microns in size.

3. A perfumed, particulate detergent and bleach composition useful for hand washing eating and cooking utensils, which composition comprises:
  - (a) at least 18% by weight of an anionic surfactant;
  - (b) from 0.5% to 3% by weight of a blooming perfume composition that contains
    - i) at least four different blooming perfume ingredients, each of which ingredients has a boiling point of 260°C or lower and a calculated  $\log_{10}$  of its octanol/water partition coefficient, P, of 3 or higher; and
    - ii) at least two different delayed blooming perfume ingredients, each of which ingredients has a boiling point of 260°C or lower and a  $\log_{10}$  of its octanol/water partition coefficient, P, of less than 3;with the proviso that when said blooming perfume composition is present as part of a cyclodextrin/perfume complex, the particles of said complex are less than 12 microns in size;
  - (c) optionally a chlorine bleach material which provides from 0% to 4% available chlorine;
  - (d) from 0% to 10% moisture; and
  - (e) a remainder being all components of the composition other than (a) through (d), the remainder comprising at least 80%, preferably at least 90%, solid materials selected from builders, fillers, and mixtures thereof.
4. A perfumed, dry particulate detergent composition useful for hand washing eating and cooking utensils, which composition comprises:
  - (a) from 10% to 40% by weight of an anionic surfactant selected from alkylbenzene sulfonates, alkyl sulfates and alkylpolyethoxylate sulfates;
  - (b) from 2% to 40% by weight of a phosphorous-containing builder selected from trisodium phosphate, tetrasodium pyrophosphate, sodium tripolyphosphate and sodium hexametaphosphate;
  - (c) from 5% to 15% by weight of a silicate builder having an  $\text{SiO}_2\text{:Na}_2\text{O}$  ratio of from 1.6:1 to 3.2:1; and

- (d) from 0.1% to 2% of a blooming perfume composition that contains at least five blooming perfume ingredients selected from the perfume materials set forth in Table 1 in the specification, with the proviso that when said blooming perfume composition is present as part of a cyclodextrin/perfume complex, the particles of said complex are less than 12 microns in size.
5. A perfumed, dry particulate detergent composition useful for hand washing eating and cooking utensils, which composition comprises:
- (a) from 10% to 40% by weight of an anionic surfactant selected from alkylbenzene sulfonates, alkyl sulfates and alkylpolyethoxylate sulfates;
  - (b) from 2% to 40% by weight of a phosphorous-containing builder selected from trisodium phosphate, tetrasodium pyrophosphate, sodium tripolyphosphate and sodium hexametaphosphate;
  - (c) from 5% to 15% by weight of a silicate builder having an  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio of from 1.6:1 to 3.2:1; and
  - (d) from 0.1% to 2% of a blooming perfume composition that contains
    - i) at least four blooming perfume ingredients selected from the perfume materials set forth in Table 1 of the specification; and
    - ii) at least two delayed blooming perfume ingredients selected from the perfume materials set forth in Table 2 of the specification;with the proviso that when said blooming perfume composition is present as part of a cyclodextrin/perfume complex, the particles of said complex are less than 12 microns in size.
6. A composition according to any of Claims 1-5 wherein
- (a) the blooming perfume composition comprises at least 8 different blooming perfume ingredients;
  - (b) each of the blooming perfume ingredients used in the blooming perfume compositions has a boiling point of  $250^\circ\text{C}$  or lower and a  $\log_{10}$  of its octanol/water partition coefficient, P, of 3.2 or higher; and

- (c) the blooming perfume composition comprises at least 50% by weight of said blooming perfume composition of said blooming perfume ingredients.
- 
- 7. A composition according to any of Claims 1-6 wherein said blooming perfume composition is incorporated into said detergent composition in the form of moisture-activated, encapsulated perfume particles, preferably said moisture-activated, encapsulated perfume particles being in the form of cyclodextrin/perfume complexes or water-soluble cellular matrix perfume microcapsules.
  - 8. A composition according to any of Claims 1-7 wherein
    - (a) the blooming perfume composition also comprises at least three different delayed blooming perfume ingredients; and
    - (b) the weight ratio of blooming perfume ingredients to delayed blooming perfume ingredients is at least 1.
  - 9. A composition according to any of Claims 1-8 which additionally contains a chlorine bleach material which provides from 0.05% to 1% available chlorine.
  - 10. A method for hand washing eating and cooking utensils using a perfumed dishwashing detergent composition, which method comprises manually contacting the utensils to be washed with an aqueous washing solution formed from a perfumed particulate detergent composition of any of Claims 1-9.



Application No: GB 9705617.0  
Claims searched: 1 to 10

Examiner: Michael Conlon  
Date of search: 11 June 1997

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C5D (DHD, DHZ, DJX)

Int Cl (Ed.6): C11D

Other: Online: WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
A	GB2303789 A (Procter & Gamble) Examples III to V	1
A	EP0430315 A2 (Unilever) page 4 lines 15 to 30 and the Examples	1
A	EP0392608 A2 (Procter & Gamble) the Examples	1
A	EP0299561 A2 (Unilever) pages 16 and 17	1
A	WO95/13345 A1 (Procter & Gamble)	1
A	WO93/05136 A1 (Procter & Gamble)	1

X Document indicating lack of novelty or inventive step  
Y Document indicating lack of inventive step if combined with one or more other documents of same category.

& Member of the same patent family

A Document indicating technological background and/or state of the art.  
P Document published on or after the declared priority date but before the filing date of this invention.  
E Patent document published on or after, but with priority date earlier than, the filing date of this application.

